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Subject: Final Report  
Grant N00014-93-1-0920  
TEES Project 43400 EE

Please find attached, two copies of the final report for the referenced grant. If you should have questions concerning the report, please contact me at (409) 845-1264 or by e-mail at dhollingsworth@tamu.edu.

Sincerely,

David Hollingsworth  
Assistant Director

Attachment

xc: J. Humphries

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DEPARTMENT OF ELECTRICAL ENGINEERING TEXAS A&M UNIVERSITY

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MEMORANDUM

February 4, 1994

**TO:** Dr. David Hollingsworth  
Assistant Director  
TEES Contacts & Grants  
308 WERC

**FROM:** Dr. R. K. Pandey *R. K. Pandey*

**SUBJECT:** Final Report for "Electrooptic Crystal Growth and Properties", ONR,  
Project No. 43400 EE

Funding made available for this project was used to send two graduate students (Mr. Pradeep Jana and Mr. V. G. Kallur) to attend the IMF '8 (International Meeting on Ferroelectricity) to present their papers. This meeting took place in Gaithersburg, MD between August 8-13, 1993.

The two papers were delivered at the meeting and full papers were prepared for publication in the Proceedings of IMF '8. The are enclosed here. The papers have been accepted for publication after the review process.

Enclosures: 2

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## CRYSTAL GROWTH AND PROPERTIES OF A NEW MEMBER OF Pb-K-NIOBATE SERIES

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**ABSTRACT** A new member in the tungsten-bronze family of ferroelectric lead-potassium-niobate (PKN), with general formula  $\text{Pb}_{1-x}\text{K}_x\text{Nb}_2\text{O}_6$ , has been grown as bulk single crystal. Growth of PKN with charge composition  $x = 0.23$  has been achieved using the Czochralski technique of crystal pulling. Large diameter boules were grown in platinum crucibles at temperatures between 1280 °C and 1300 °C. Crystallographic studies were conducted using X-ray diffraction techniques. The samples were characterized for ferroelectric properties between 25 °C and 600 °C and for optical absorption. This paper presents the crystal synthesis and the results of ferroelectric and optical characterization.

### INTRODUCTION

Ferroelectric tungsten-bronze (TB) oxides in general exhibit ferroelasticity and are attractive for electrooptic and pyroelectric devices<sup>1</sup>. Single crystals of PKN with  $x = 0.20$  have been found to possess attractive physical properties which make it a very desirable substrate material for surface acoustic wave (SAW) devices<sup>2,3</sup>. Current materials for this application such as  $\alpha$ -quartz and lithium niobate are of limited interest because of their intrinsic physical properties in the upper frequency limit of operation<sup>4</sup>. The largest electromechanical coupling factors ever observed in a TB structure are those of  $\text{Pb}_2\text{KNb}_5\text{O}_{15}$  crystals with  $\kappa_{15} = 0.69$  and  $\kappa_{24} = 0.73$ <sup>5</sup>. However PKN, though satisfactory in performance over a much wider frequency bandwidth, has been shown to contain innumerable cracks all across the bulk when synthesized as single crystals<sup>5,6</sup>. This drastically limits its usefulness for fabrication of devices for practical applications. Thus there is a growing need for materials which may exhibit superior properties of PKN with  $x = 0.20$  but can be grown as large single crystals without mechanical flaws.

Pb-K-niobate ( $\text{Pb}_{1-x}\text{K}_x\text{Nb}_2\text{O}_6$ ) series is a limited solid solution between Pb-niobate ( $\text{PbNb}_2\text{O}_6$ ) and K-niobate ( $\text{KNbO}_3$ ) for  $x$  varying from 0 to 0.34<sup>7</sup>. Two new

members of the PKN series with  $x = 0.23$  and  $x = 0.34$  were processed and pressed into pellet forms. These materials have been found to exhibit comparable ferroelectric properties to those of PKN with  $x = 0.2$ <sup>8</sup>. PKN with  $x = 0.23$  melts over a very narrow range of temperature as shown by the differential thermal analysis<sup>9</sup>. Also, the Curie temperature for this composition was found to be significantly lower than that of PKN with  $x = 0.20$ . Hence powder charge of this composition was prepared for the purpose of crystal growth.

### CRYSTAL GROWTH

Powder charge of PKN  $x = 0.23$  was prepared from highly pure  $\text{PbO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{K}_2\text{CO}_3$ <sup>8</sup>. Crystal growth experiment was conducted in a 25 cc platinum ODS crucible in an inductively heated furnace by the Czochralski technique of crystal pulling. Platinum wire was used to initiate nucleation for earlier experiments. For subsequent experiments crystalline portions of grown boules from the previous experiments were used as seeds. The platinum crucible was packed with PKN charge, mounted in the furnace and the growth chamber was sealed. An oxygen atmosphere was maintained. Heating rate was about 600 °C per hour. At about 1280 °C melt started appearing at the walls. Once all the charge had molten brown vapors rose from the melt. This is believed to be vapors of  $\text{PbO}$  as reported previously<sup>5,6</sup>. The furnace was maintained at a constant temperature to homogenize the melt. Seed rod was then lowered and nucleation was initiated on the seed. Several such experiments were conducted under different growth conditions of pulling rates, rotation speeds and oxygen pressure.

### CHARACTERIZATION AND RESULTS

Several  $\text{Pb}_{1-x}\text{K}_x\text{Nb}_2\text{O}_6$  crystals were grown with a nominal composition of  $x = 0.23$ . Boule size varied from about 6 mm to 20 mm in diameter. Length varied from about 3 mm to 40 mm. They weighed from about 10 g to 40 g. Density of this crystal was measured to be  $6.25 \times 10^3 \text{ kg/m}^3$ . Optimum growth conditions are as follows: pulling rate of 4 mm/hr, crucible rotation of 10-15 rpm and melt temperature between 1280 °C and 1300 °C. One such crystal is shown in fig. 1.

The crystals exhibited a lot of cracks all across the boule. It is believed that cracking is an inherent property of this material grown by this technique<sup>2,4,5</sup>. The boule shattered upon application of pressure due to the presence of such cracks. Some of the crystallites were of dimension 5 x 4 x 3 mm and they were used for our studies. The color of the boules was green to brown. However, the crystals were brownish yellow to brownish orange upon breaking. They were mostly transparent to visible light. X-ray diffraction studies were carried out with  $\text{Cu-K}\alpha$  radiation. In fig. 2 Laue

back reflection pattern is shown. The elongation of spots suggests the presence of large strain in the crystal<sup>10</sup>. From single crystal rotation technique the values of the lattice constants are determined to be:  $a = 17.762 \text{ \AA}$ ,  $b = 18.020 \text{ \AA}$  and  $c = 3.9147 \text{ \AA}$ . This is in good agreement with the values reported for powder charge for PKN with  $x = 0.23$ <sup>8</sup>.

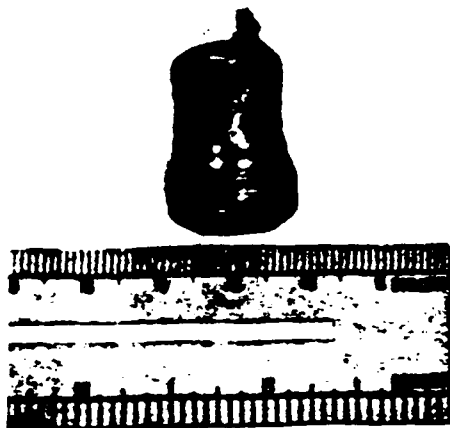


FIGURE 1 Photograph of PKN crystal with  $x = 0.23$



FIGURE 2 Laue X-ray pattern of PKN with  $x = 0.23$

All properties were studied on samples perpendicular to the  $c$ -axis. Thin samples were obtained by slicing the boule with a diamond saw. They could not be polished due to their fragile nature. The surfaces were gold sputtered for electrical contact.

#### Ferroelectric Properties

It was not possible to pole the PKN crystal with any applied electrical field. The extremely large coercive field - greater than even the breakdown field<sup>11</sup> - does not allow a stable hysteresis loop to be generated below the Curie temperature. The polarization value continuously changes due to the switching of domains in the sample. Thus, the hysteresis behavior alternates constantly between a narrow loop and a wide loop. However, in the paraelectric state a linear relationship between the polarization and externally applied electric field is displayed.

Fig. 3 shows the relative dielectric constant of PKN crystal with  $x = 0.23$  as a function of temperature measured at 1 kHz. It can be seen that there is a sharp transition at the Curie point of  $397^\circ\text{C}$ . This is in conformity with the data on the polycrystalline pellets and is a significant evidence for the equality in composition between charge and the crystal. Peak dielectric constant is found to be the largest value reported for any derivative of lead metaniobate. The Curie-Weiss temperature is at  $385$

$^{\circ}\text{C}$  and the Curie-Weiss constant is  $4.4 \times 10^4 \text{ }^{\circ}\text{C}$ . The a.c. conductivity of PKN is plotted in fig. 4. The change of slope for the second time at  $410 \text{ }^{\circ}\text{C}$  is perhaps due to the presence of ferroelastic transition. Such a phenomenon has already been reported for  $x = 0.20$  <sup>2,5</sup>. The existence of a high conductivity, and hence losses, is evident from the large hysteresis loop generated for PKN.

The pyroelectric coefficient increases steadily with rising temperature. Cooling rate was  $4 \text{ }^{\circ}\text{C}/\text{min}$ . Well above the ferroelectric transition the current generated continues to mount but with a steeper slope. This is perhaps due to the high absorption of the incident radiation, as shown by the absorption spectra.

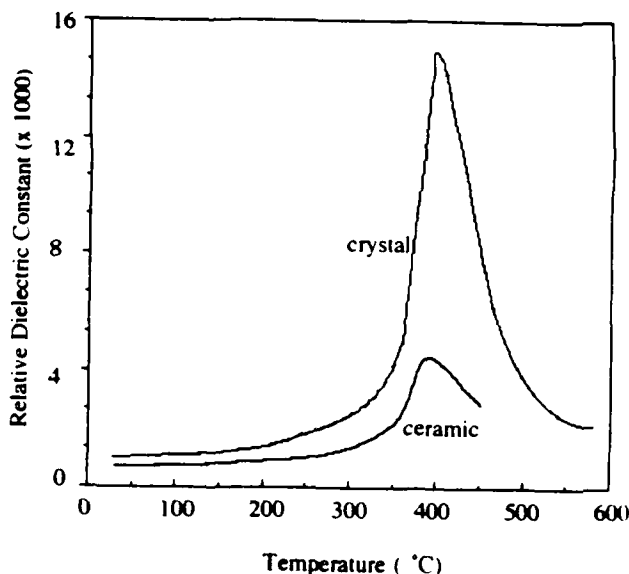


FIGURE 3 Relative Dielectric Constant as a function of temperature of PKN with  $x = 0.23$

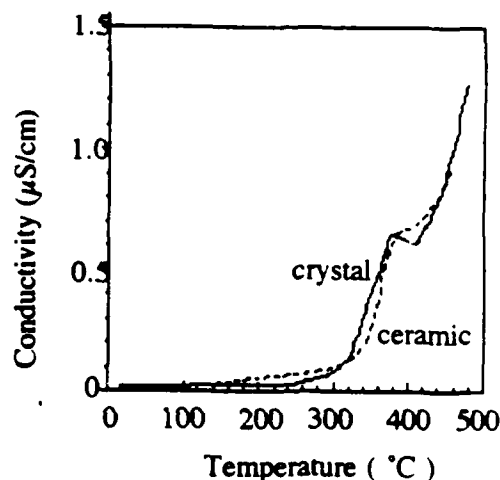


FIGURE 4 Thermal behavior of a.c. conductivity of PKN with  $x = 0.23$

The Curie point of Pb-K-niobates show strong dependence on  $x$  and it is shown in fig. 5. This dependence of  $x$  can be represented by the following relationship:

$$T_c = 570 - (97.498)x - (2498)x^2 \quad (1)$$

A large number of ferroelectric and ferroelastic domains were also observed optically. They belonged to  $90^{\circ}$ ,  $135^{\circ}$  and  $180^{\circ}$  types. Under a polarizer the dark and bright fields alternated between red and green colors.

#### Optical Absorption

Absorbance nature of PKN was measured over the wavelength range of  $0.5 \mu\text{m} - 25 \mu\text{m}$  by Fourier Transform Infrared Spectrometer (FTIR). This corresponds to the electromagnetic range of blue to deep infrared and is plotted in fig. 6. The increase in

absorbance is sharp in the larger wavelength region (between  $7.5\ \mu\text{m}$  and  $25\ \mu\text{m}$ ). This is most likely due to phonon reststrahlen bands which do not allow radiation to be transmitted through the sample. The absorbance peaks around  $5.4\ \mu\text{m}$ ,  $5.7\ \mu\text{m}$ ,  $6.9\ \mu\text{m}$  and  $7.5\ \mu\text{m}$  are also probably vibrational in nature, but maybe due to two-phonon processes. This is because single phonon processes occur at frequencies inside the reststrahlen bands. Over the spectral range of about  $0.5\ \mu\text{m}$  to  $5\ \mu\text{m}$  the absorbance of the material increases linearly with frequency. The singularity at  $2.85\ \mu\text{m}$  has been observed in other ferroelectric materials<sup>12</sup> and is attributed to OH stretching mode. This nearly linear increase indicates that there is no definite bandgap in the range of frequencies in which this study was conducted. Instead, the data would indicate a broad band, most likely electronic in nature, which has a steadily increasing density of states with frequency. Below  $0.5\ \mu\text{m}$  the absorbance seems to flatten out. This behavior is qualitatively similar to that observed in the absorption spectra of KTN crystals<sup>12</sup>.

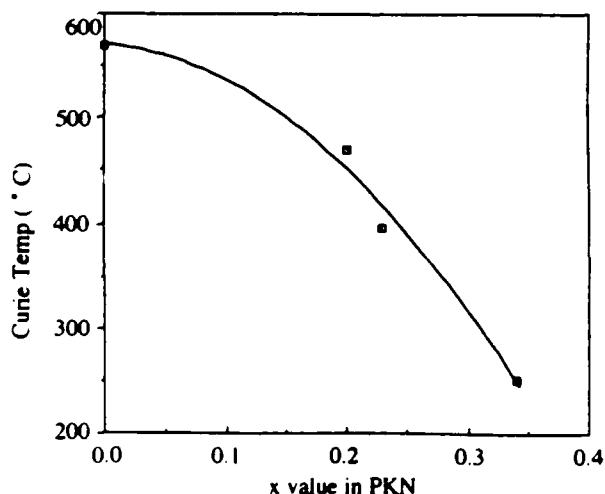


FIGURE 5 Compositional dependence of Curie temperature for PKN

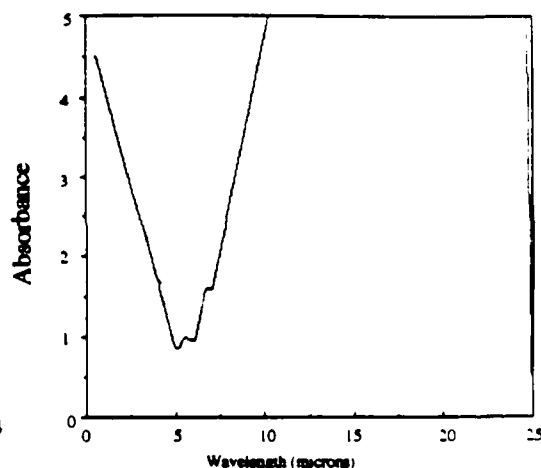


FIGURE 6 Absorbance spectra of PKN with  $x = 0.23$

When our PKN specimens are heated to over  $100\ ^\circ\text{C}$  they become highly transparent with a light yellow color. When allowed to cool to room temperature it returns to its normal state. However if after heating, the sample is stored in a light tight container it retains its property of being more transparent. This is perhaps due to photochromic activity of color centers<sup>13</sup>. PKN is believed to be optically active because of this reason.

### CONCLUSIONS

Single crystals of Pb-K-niobate crystals have been synthesized from a charge of composition  $x = 0.23$  by the technique of Czochralski pulling. Although numerous

cracks appeared in the boule it is encouraging to note that a new member of the PKN series has been synthesized. By identification of a better growth technique and slower rates of cooling it is believed that these cracks can be avoided and large single crystal boules can be grown. The properties measured represent an improvement over the previously grown crystals. Table 1 gives the comparison of properties of PKN with different compositions.

Table 1 Comparison of properties of different PKN members

PKN	Parameter	x = 0.20 crystal <sup>5,13</sup>	x = 0.23 ceramic <sup>7</sup>	x = 0.23 crystal	x = 0.34 ceramic <sup>7</sup>
Lattice	a	17.723	17.192	17.762	17.526
Constants (Å)	b	17.987	18.096	18.020	18.443
	c	3.895	3.867	3.9147	3.898
T <sub>m</sub>	(°C)	1300	1280	1280	1220
T <sub>c</sub>	(°C)	469 ± 4	396 ± 2	397 ± 1	242 ± 1
Density	(g/cc)	6.12	5.167	6.25	5.6
Dielectric Constant	at 25 °C	1500	498	1000	858
	at T <sub>c</sub>	12500	4570	15000	2914
C-W Temp.	(°C)	450	N/A	385	N/A
C-W Const.	(°C)	2.5 × 10 <sup>4</sup>	N/A	4.4 × 10 <sup>4</sup>	N/A
σ (μS/cm)	at 25 °C	0.012	0.0095	0.0095	0.0096
p @ T <sub>c</sub>	(μC/cm <sup>2</sup> °C)	N/A	N/A	0.225	N/A

N/A - data not available

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## CRYSTAL GROWTH AND PROPERTIES OF POTASSIUM TANTALATE NIOBATE, $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ , FERROELECTRIC

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**Abstract** Bulk single crystals of potassium tantalate niobate,  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ , ferroelectric with different values of Ta/Nb ratios have been grown by temperature gradient transport technique (TGTT). The samples with different values of  $x$  were characterized by measuring their spontaneous polarization, dielectric constant and losses, pyroelectric coefficients, Curie temperatures and lattice constants. This paper presents the results of the crystal growth experiments, ferroelectric characterization techniques and properties of potassium tantalate niobate crystals.

### INTRODUCTION

Potassium tantalate niobate,  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ , is a well known ferroelectric solid solution between potassium tantalate,  $\text{KTaO}_3$  and potassium niobate,  $\text{KNbO}_3$  perovskites. Both these materials exhibit ferroelectricity with the Curie point,  $T_C$ , at 700 K for  $\text{KNbO}_3$ ; and at 13 K for  $\text{KTaO}_3$ .<sup>1</sup> Potassium tantalate niobates, commonly referred to as KTN, have been identified for a large number of applications including electro-optic modulation and deflection, second harmonic generation, IR radiation detection and holographic data storage.<sup>2</sup> Because of the nonavailability of high quality single crystals of KTN having the ferroelectric Curie point above the room temperature, its technological potential has not been completely exploited. The method of TGTT for crystal growth is found to be extremely useful for producing relatively large crystals of KTN with practically no compositional gradient.<sup>2,3</sup> Highly homogeneous crystals of KTN with  $x = 0.19, 0.35$  and  $0.42$  have been grown by us; and specimens have been used for determining their fundamental ferroelectric parameters.

### CRYSTAL GROWTH

Previous attempts to grow large crystals of KTN produced only small samples with sufficient homogeneity for device applications.<sup>3</sup> TGTT growth takes place at a constant temperature yielding high optical quality large bulk crystals of KTN. Charge for the crystal growth was prepared using high purity potassium carbonate ( $\text{K}_2\text{CO}_3$ ), niobium

pentoxide ( $\text{Nb}_2\text{O}_5$ ), tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ) and a small amount of tin oxide ( $\text{SnO}_2$ ) to enhance clarity in the crystals. The charge is then solid state reacted and packed into a Pt / 10% Rh crucible.<sup>2</sup>

The crucible with the well reacted charge was placed in an inductively coupled furnace which was enclosed in a stainless steel chamber with a provision for air to flow slowly during the growth. The furnace was profiled in such a way that there existed approximately  $3^\circ\text{C}$  gradient from the top to the bottom of the crucible. Once the charge was molten it was soaked sufficiently to make it homogeneous. The melt was slowly cooled till it reached approximately  $10^\circ\text{C}$  below growth temperature and held there. Supersaturation caused nutrient material to deposit at the bottom of the crucible. After the accumulation of sufficient nutrient material the crucible temperature was raised to the growth temperature and a seed was introduced. Convective currents set within the melt because of the gradient facilitated the growth on the seed. Crucible was rotated at about 10 rpm and the seed was rotated counter to crucible rotation between 30 to 70 rpm. Once the crystal started to grow the seed was pulled at a rate of 1 mm/hr. The size of the crystal grown depends on the amount of nutrient material available. After the crystal was pulled out of the melt, it was cooled to room temperature slowly. Compositional analysis confirmed the stoichiometry of the crystals and the absence of compositional gradient. Additional advantage of this technique is that different compositions of KTN can be grown using the same charge just by varying growth temperatures. Crystals of sizes upto 1.5 cm X 1.5 cm X 1.5 cm were grown repeatedly by this method from a 50 cc crucible. Fig. 1 shows one of the crystals grown.<sup>3</sup>

### CHARACTERIZATION

X-ray analysis was performed to determine the lattice constants. For dielectric characterization specimens of 5 mm X 5 mm X 5 mm, in size were cut from the boules. Sample surfaces were polished using a Buehler polisher and electroded.

Three different compositions of KTN single crystals with  $x = 0.19, 0.35$  and  $0.42$  were characterized. The Laue pattern of  $x = 0.42$  crystal is shown in fig. 2. Lattice parameters of these crystals are given in table 1.<sup>4</sup> Ferroelectric transition of KTN with  $x = 0.19, 0.35$  and  $0.42$  were determined to be 173 K, 273 K and 320 K, respectively from the temperature dependence of relative dielectric constant ( $\epsilon_r$ ) and pyroelectric coefficient ( $p$ ). The Curie point is strongly dependent upon the niobium concentration  $x$  in KTN. It obeys the relationship  $T_c = 676 + 32x$  as reported.<sup>5</sup>

A two stage thermoelectric cooler was utilized to measure the ferroelectric data of  $x = 0.35$  and  $0.42$  samples. Measurements on  $x = 0.19$  crystal was performed with a APD cryostat since the sample had to be cooled to low temperatures. Crystals were

poled by applying a DC bias of 2 - 2.5 kV/cm across them and cooling through their Curie temperatures.



FIGURE 1 KTN single crystal.

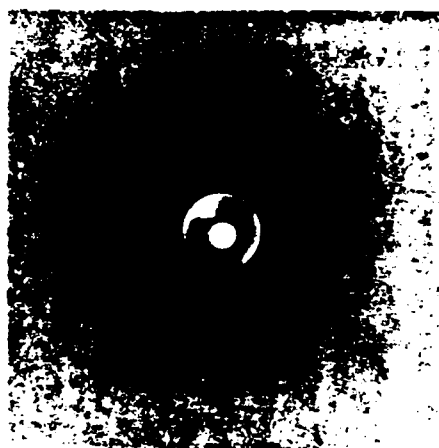


FIGURE 2 Laue pattern of KTN with  $x = 0.42$ .

Dielectric constant measurements on  $x = 0.42$  and  $0.35$  samples were performed over a temperature range with an ESI 253 impedance meter which uses a reference signal of 1V at 1KHz frequency. The plots of the relative dielectric constant ( $\epsilon_r$ ) vs temperature for both the samples are shown in fig. 3. The larger peaks in the plots correspond to the Curie temperature representing a transition from cubic to tetragonal phase as the sample is cooled down. The smaller peaks correspond to the lower order transition representing phase change from tetragonal to orthorhombic like in any other perovskite structure. The crystal with  $x = 0.42$  has the peak  $\epsilon_r$  of 12000 at  $T_c = 320$  K; and  $x = 0.35$  of 12500 at  $T_c = 273$  K. These values are in agreement with the values reported by Triebwasser.<sup>1</sup> The  $x = 0.19$  sample exhibited a dielectric constant transition very similar to that of a relaxor ferroelectric. Phase transition of  $x = 0.19$  sample at higher frequencies is accompanied by a broadening of the dielectric peak as well as a shift in the position of the transition point (Fig. 4).

AC conductance measurements were performed with the same impedance meter employed for capacitance measurements.  $\tan \delta$  or dissipation factor values calculated were in the range of 3 - 4 % which is relatively large for a ferroelectric material. This lossy nature of KTN has prevented it from being used in certain applications, particularly in pyroelectric imaging.<sup>6</sup> This can be attributed to the  $\text{SnO}_2$ -doping which enhances the leakage current. It is believed that KTN without the  $\text{SnO}_2$ -doping should have substantially lower leakage currents.

A modified Sawyer-Tower circuit which had a resistor in series with the sample to compensate for its losses was integrated and used to measure the hysteresis and

polarization in the crystals. Hysteresis loops were observed on a dual channel Tektronix 455 oscilloscope with a 60 Hz signal. Room temperature hysteresis in  $x = 0.42$  sample is shown in fig. 5. Polarization values measured and Curie-Weiss constants calculated are given in table 1. These values are very close to those reported in literature.<sup>7</sup>

KTN has been proposed to be a good substitute material for infrared detection provided its dielectric losses are low and leakage currents small. Dielectric losses reduces the voltage responsivity in the material for the incident signal.<sup>8</sup> Fig. 6 shows pyroelectric behavior of  $x = 0.42$  sample before poling and after poling. It can be seen from this figure how poling changes the magnitude of pyroelectric coefficient values as well as the order of transition. Direct measurement technique developed by Byer and Roundy<sup>9</sup> was used for the purpose of pyroelectric detection. Ferroelectric properties of KTN crystals measured are tabulated in table 1.

TABLE 1 Properties of KTN crystals of different compositions.

Properties	$x = 0.42$	$x = 0.35$	$x = 0.19$
$T_c$ (K)	320	273	173
Crystal structure (@ room temperature)	Tetragonal	Cubic	Cubic
Lattice parameters (@ room temperature)	$a=b=3.9977\text{\AA}$ $c=4.0081\text{\AA}$	$a = b = c$ $= 3.9983\text{\AA}$	$a = b = c$ $= 3.9941\text{\AA}$
$(P_{rem})_{peak}$ ( $\mu\text{C}/\text{cm}^2$ )	5.6	3	4
$P_{rem}$ ( $\mu\text{C}/\text{cm}^2$ ) (@ room temperature)	5.5	-	-
$E_c$ (kV/cm) (@ room temperature)	0.88	-	-
$(\epsilon_r)_{peak}$	(12000) <sub>1KHz</sub>	(12500) <sub>1KHz</sub>	(9200) <sub>50Hz</sub>
$\epsilon_r$ (@ room temperature)	(3640) <sub>1KHz</sub>	(4800) <sub>1KHz</sub>	(3500) <sub>50Hz</sub>
Losses	0.03 - 0.04	0.04 - 0.06	0.04 - 0.06
Curie-Weiss constant (K)	$2.38 \times 10^5$	$1.26 \times 10^5$	$3.6 \times 10^5$
Pyroelectric coefficient @ $T_c$ ( $\mu\text{C}/\text{cm}^2\text{-K}$ )	0.3	0.08	-

The unique feature of KTN is that it undergoes different orders of transition over its entire solid solution range. As the concentration of niobium is increased the transition tends toward the first order.

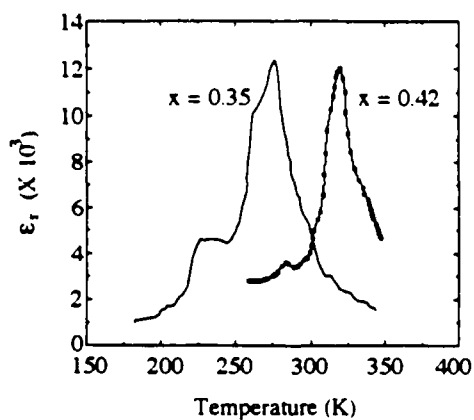


FIGURE 3 Relative dielectric constant vs temperature plot of KTN crystals.

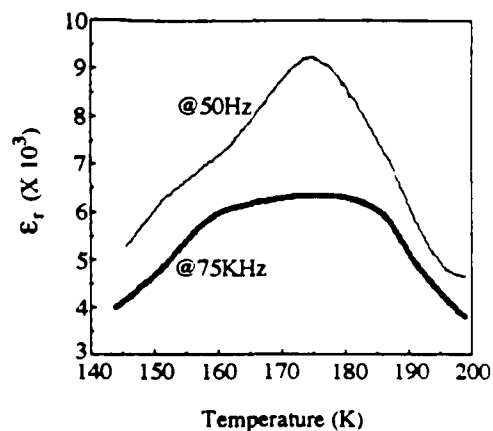


FIGURE 4 Relaxor behavior observed in  $x = 0.19$  crystal.

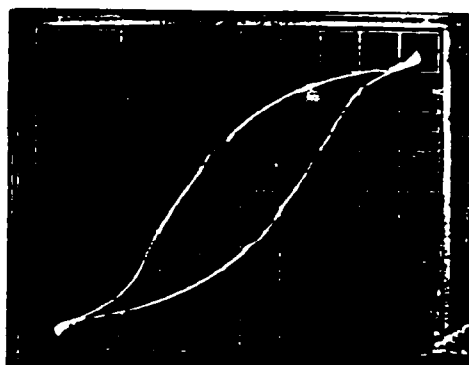


FIGURE 5 Hysteresis loop of  $x = 0.42$  crystal at 300 K.

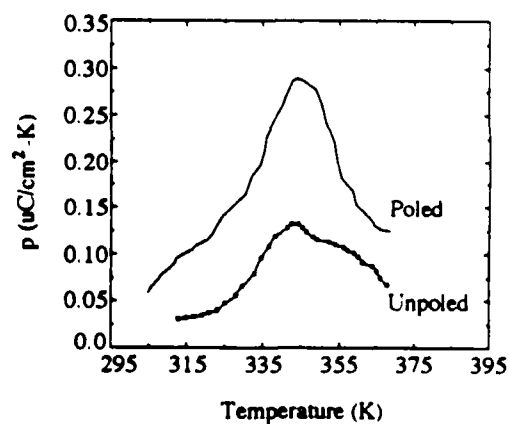


FIGURE 6 Pyroelectric behavior of  $x = 0.42$  crystal.

## CONCLUSIONS

Temperature gradient transport technique is identified to be a suitable method for the growth of high quality bulk single crystals of KTN with minimal compositional variance thereby overcoming the problems that were encountered previously. This technique has been utilized in our laboratory for growth of KTN crystals with variable compositions to match the needs of different applications with the same initial charge. Characterization of the crystals establish their ferroelectric nature and indicate KTN samples to possess some properties at par with leading ferroelectrics like BaTiO<sub>3</sub> and PZT which are widely used currently. KTN crystals with  $x = 0.42$  and  $0.35$  are found to undergo a second order transition whereas crystals with  $x = 0.19$  exhibits a diffused transition.

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